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3-(Dihydroxyboryl)anilinium 6-carboxypyridine-2-carboxylate

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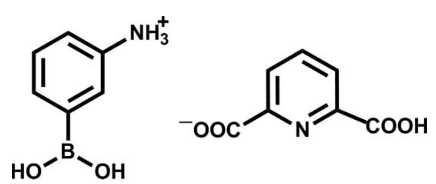
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 13.0.

In the anion of the title molecular salt, $C_6H_9BNO_2^+\cdot C_7H_4NO_4^-$, the dihedral angles between the $-COO^{2-}$ and $-CO_2H$ groups and their attached ring are 4.02 (13) and 21.41 (10)°, respectively. The B atom in the cation adopts a *syn–syn* geometry and the dihedral angle between the $-B(OH)_2$ group and its attached ring is 11.06 (5)°. In the crystal, O—H···O, N—H···O and N—H···N hydrogen bonds link the components into a three-dimensional network.

Related literature

For general background, see: Hall (2005). For related structures, see: Li *et al.* (1995); SeethaLekshmi & Pedireddi (2006); Sokolov & MacGillivray (2006); Vega *et al.* (2010).



Experimental

Crystal data

$C_6H_9BNO_2^+\cdot C_7H_4NO_4^-$
M_r = 304.06
Monoclinic, $P2_1/n$
a = 7.7065 (6) Å
b = 14.0473 (10) Å
c = 13.0852 (10) Å
β = 106.963 (1)°
V = 1354.92 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 K
0.28 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.958, T_{max} = 0.989
8330 measured reflections
2677 independent reflections
2260 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 1.05
2677 reflections
206 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O3^{i}	0.96 (2)	1.47 (3)	2.429 (2)	173 (2)
N2—H2A···O1^{i}	0.89	2.42	2.808 (2)	107
N2—H2A···O3^{i}	0.89	2.42	2.835 (2)	109
N2—H2A···N1^{i}	0.89	2.08	2.955 (2)	169
N2—H2B···O3^{i}	0.89	2.49	2.835 (2)	104
N2—H2B···O2	0.89	2.03	2.907 (2)	170
N2—H2C···O6^{ii}	0.89	2.15	2.947 (2)	149
O5—H5···O2^{iii}	0.82	2.04	2.712 (2)	139
O6—H6···O4^{iv}	0.82	1.91	2.694 (2)	158

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $-x+1, -y+2, -z$; (iv) $x-2, y, z-1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: Mercury (Macrae *et al.*, 2006), *PLATON* (Spek, 2009), *SHELXL97* and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5313).

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supplementary materials

Acta Cryst. (2012). E**68**, o2559 [doi:10.1107/S1600536812031790]

3-(Dihydroxyboryl)anilinium 6-carboxypyridine-2-carboxylate

Chunhua Ge, Xiangdong Zhang, Rui Zhang and Chenglong Zhang

Comment

Boronic acid and its derivates have attracted great interest in various areas of materials science, catalysis, surface chemistry, organic synthesis, biochemistry, and luminosity (Hall, 2005). Boronic acid has been utilized to contructed covalent macrocycles compounds and organic frameworks as building block. Intermolecular interactions of boronic acid have now been well explored in the rapid development of organic supramolecular assemblies. A large variety of boronic acids have shown the application as new building blocks in crystal engineering through hydrogen-bonding interactions. 4-Carboxyphenylboronic acid was shown to produce second-sphere coordination networks with transition metals (SeethaLekshmi & Pedireddi, 2006). Cocrystallization of *trans*-1,2-bis(4-pyridyl)ethylene with phenylboronic acid could generate one-dimensional hydrogen bonded infinite ladder (Sokolov & MacGillivray, 2006). In the crystal of 3-amino-phenyl boronic acid hydrochloride, each chloride ion is connected four organic ions by N—H···Cl and O—H···Cl hydrogen bonds (Li *et al.*, 1995). Bis[3-(dihydroxyboryl)anilinium] sulfate can provide a complex three-dimensional supramolecular network by hydrogen bonds (Vega *et al.*, 2010).

Here, we present the title compound - an organic salt of 3-(dihydroxyboryl)anilinium and 6-carboxypyridine-2-carboxylate (Fig. 1). In the crystal, intermolecular O—H···O, N—H···O and N—H···N interactions (Table 1) generate hydrogen-bonding network, which link cations and anions into three-dimensional structure.

Experimental

An ethanolic solution of 2,6-pyridinedicarboxylic acid(0.5 mmol in 10 ml e thanol)was added dropwise to 3-aminophenyl boronic acid monohydrate (0.5 mmol in 5 ml e thanol) with stirring. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature.

Refinement

Atom H1A was located in a difference Fourier map and refined with a distance restraint O—H = 0.96 (2) Å. All other H atoms were positioned geometrically and refined using riding model, with C—H = 0.93 Å, O—H = 0.82 Å, N—H = 0.89 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(O).

Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: Mercury (Macrae *et al.*, 2006), *PLATON* (Spek, 2009), *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999).

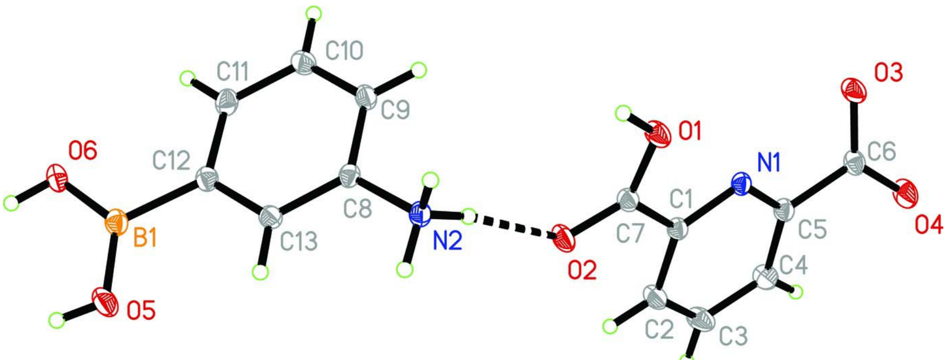

Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

3-(Dihydroxyboryl)anilinium 6-carboxypyridine-2-carboxylate

Crystal data

$C_6H_9BNO_2^+ \cdot C_7H_4NO_4^-$
$M_r = 304.06$
Monoclinic, $P2_1/n$
Hall symbol: -P2yn
$a = 7.7065$ (6) Å
$b = 14.0473$ (10) Å
$c = 13.0852$ (10) Å
$\beta = 106.963$ (1)°
$V = 1354.92$ (18) Å^3
$Z = 4$
$F(000) = 632$
$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 58 reflections
$\theta = 2.3$–22.7°
$\mu = 0.12$ mm^{-1}
$T = 293$ K
Block, colourless
0.28 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.958$, $T_{max} = 0.989$
8330 measured reflections
2677 independent reflections
2260 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.2°$
$h = -9 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.102$
$S = 1.05$
2677 reflections
206 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O2	0.99515 (15)	0.89532 (8)	0.27933 (8)	0.0301 (3)
B1	0.1026 (2)	0.91402 (12)	−0.06619 (13)	0.0257 (4)
C1	1.19186 (19)	0.93213 (10)	0.45205 (11)	0.0227 (3)
C2	1.1728 (2)	1.02978 (11)	0.43673 (12)	0.0300 (4)
H2	1.0986	1.0544	0.3729	0.036*
C3	1.2659 (2)	1.08965 (11)	0.51780 (14)	0.0363 (4)
H3	1.2534	1.1553	0.5101	0.044*
C4	1.3776 (2)	1.05063 (11)	0.61038 (13)	0.0319 (4)
H4	1.4459	1.0894	0.6650	0.038*
C5	1.38602 (19)	0.95208 (10)	0.62036 (12)	0.0248 (3)
C6	1.5061 (2)	0.90725 (10)	0.72088 (12)	0.0266 (3)
C7	1.09722 (19)	0.86419 (10)	0.36402 (11)	0.0233 (3)
C8	0.57150 (19)	0.81556 (10)	0.09336 (11)	0.0212 (3)
C9	0.5358 (2)	0.76762 (10)	0.17760 (12)	0.0246 (3)
H9	0.6274	0.7350	0.2274	0.030*
C10	0.3611 (2)	0.76933 (11)	0.18593 (12)	0.0280 (3)
H10	0.3345	0.7388	0.2426	0.034*
C11	0.2256 (2)	0.81672 (11)	0.10949 (12)	0.0273 (3)
H11	0.1085	0.8168	0.1157	0.033*
C12	0.2593 (2)	0.86417 (10)	0.02364 (12)	0.0241 (3)
C13	0.43773 (19)	0.86366 (10)	0.01759 (11)	0.0230 (3)
H13	0.4662	0.8958	−0.0376	0.028*
H1A	1.070 (4)	0.7337 (19)	0.329 (2)	0.103 (10)*
N1	1.29358 (16)	0.89300 (8)	0.54318 (9)	0.0222 (3)
N2	0.75722 (16)	0.81145 (8)	0.08587 (10)	0.0230 (3)
H2A	0.7832	0.7520	0.0719	0.034*
H2B	0.8341	0.8302	0.1475	0.034*
H2C	0.7673	0.8497	0.0337	0.034*
O1	1.13249 (15)	0.77632 (8)	0.38493 (8)	0.0309 (3)
O3	1.46409 (15)	0.82127 (8)	0.73569 (9)	0.0334 (3)
O4	1.63185 (16)	0.95337 (9)	0.77863 (10)	0.0424 (3)
O5	0.15502 (15)	0.96244 (9)	−0.14174 (9)	0.0371 (3)
H5	0.0661	0.9872	−0.1837	0.056*
O6	−0.07164 (14)	0.90249 (8)	−0.06323 (8)	0.0312 (3)
H6	−0.1416	0.9245	−0.1178	0.047*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0322 (6)	0.0294 (6)	0.0216 (5)	0.0028 (4)	−0.0035 (5)	0.0030 (4)
B1	0.0264 (9)	0.0232 (8)	0.0244 (9)	0.0018 (7)	0.0023 (7)	−0.0019 (6)
C1	0.0208 (7)	0.0259 (7)	0.0204 (7)	−0.0005 (6)	0.0045 (6)	0.0007 (6)
C2	0.0350 (9)	0.0271 (8)	0.0235 (8)	0.0021 (6)	0.0016 (7)	0.0039 (6)
C3	0.0485 (10)	0.0207 (7)	0.0351 (9)	0.0004 (7)	0.0050 (8)	0.0015 (7)
C4	0.0376 (9)	0.0249 (8)	0.0277 (8)	−0.0041 (7)	0.0008 (7)	−0.0043 (6)
C5	0.0222 (7)	0.0256 (7)	0.0242 (8)	−0.0002 (6)	0.0030 (6)	−0.0014 (6)
C6	0.0263 (8)	0.0265 (8)	0.0231 (8)	0.0017 (6)	0.0014 (6)	−0.0030 (6)
C7	0.0227 (7)	0.0261 (7)	0.0203 (7)	0.0012 (6)	0.0050 (6)	0.0022 (6)
C8	0.0190 (7)	0.0210 (7)	0.0220 (7)	−0.0012 (5)	0.0033 (5)	−0.0029 (5)
C9	0.0237 (7)	0.0250 (7)	0.0216 (7)	0.0014 (6)	0.0012 (6)	0.0013 (6)
C10	0.0287 (8)	0.0318 (8)	0.0237 (8)	−0.0001 (6)	0.0080 (6)	0.0043 (6)
C11	0.0201 (7)	0.0328 (8)	0.0290 (8)	0.0016 (6)	0.0071 (6)	−0.0001 (6)
C12	0.0237 (8)	0.0217 (7)	0.0245 (8)	0.0009 (6)	0.0033 (6)	−0.0025 (6)
C13	0.0247 (8)	0.0225 (7)	0.0208 (7)	−0.0001 (6)	0.0051 (6)	0.0013 (5)
N1	0.0193 (6)	0.0241 (6)	0.0209 (6)	−0.0004 (5)	0.0024 (5)	−0.0007 (5)
N2	0.0203 (6)	0.0241 (6)	0.0223 (6)	0.0000 (5)	0.0026 (5)	−0.0001 (5)
O1	0.0382 (7)	0.0241 (5)	0.0228 (6)	0.0001 (5)	−0.0031 (5)	0.0002 (4)
O3	0.0369 (7)	0.0280 (6)	0.0261 (6)	−0.0019 (5)	−0.0052 (5)	0.0029 (4)
O4	0.0396 (7)	0.0342 (6)	0.0369 (7)	−0.0055 (5)	−0.0145 (5)	−0.0009 (5)
O5	0.0291 (6)	0.0446 (7)	0.0344 (7)	0.0090 (5)	0.0042 (5)	0.0160 (5)
O6	0.0234 (6)	0.0377 (6)	0.0270 (6)	0.0021 (5)	−0.0010 (4)	0.0063 (5)

Geometric parameters (Å, º)

O2—C7	1.2367 (17)	C8—C13	1.381 (2)
B1—O5	1.355 (2)	C8—C9	1.386 (2)
B1—O6	1.365 (2)	C8—N2	1.4640 (18)
B1—C12	1.582 (2)	C9—C10	1.382 (2)
C1—N1	1.3391 (18)	C9—H9	0.9300
C1—C2	1.388 (2)	C10—C11	1.387 (2)
C1—C7	1.510 (2)	C10—H10	0.9300
C2—C3	1.380 (2)	C11—C12	1.394 (2)
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.379 (2)	C12—C13	1.400 (2)
C3—H3	0.9300	C13—H13	0.9300
C4—C5	1.390 (2)	N2—H2A	0.8900
C4—H4	0.9300	N2—H2B	0.8900
C5—N1	1.3403 (19)	N2—H2C	0.8900
C5—C6	1.507 (2)	O1—H1A	0.963 (18)
C6—O4	1.2260 (19)	O5—H5	0.8200
C6—O3	1.2796 (19)	O6—H6	0.8200
C7—O1	1.2763 (18)		
O5—B1—O6	125.84 (14)	C9—C8—N2	117.31 (12)
O5—B1—C12	116.05 (14)	C10—C9—C8	118.56 (14)
O6—B1—C12	118.08 (13)	C10—C9—H9	120.7

N1—C1—C2	122.97 (13)	C8—C9—H9	120.7
N1—C1—C7	116.54 (12)	C9—C10—C11	119.81 (14)
C2—C1—C7	120.48 (13)	C9—C10—H10	120.1
C3—C2—C1	118.82 (14)	C11—C10—H10	120.1
C3—C2—H2	120.6	C10—C11—C12	122.15 (14)
C1—C2—H2	120.6	C10—C11—H11	118.9
C4—C3—C2	118.99 (14)	C12—C11—H11	118.9
C4—C3—H3	120.5	C11—C12—C13	117.39 (13)
C2—C3—H3	120.5	C11—C12—B1	121.94 (13)
C3—C4—C5	118.59 (14)	C13—C12—B1	120.64 (13)
C3—C4—H4	120.7	C8—C13—C12	120.12 (13)
C5—C4—H4	120.7	C8—C13—H13	119.9
N1—C5—C4	123.08 (14)	C12—C13—H13	119.9
N1—C5—C6	117.05 (13)	C1—N1—C5	117.46 (12)
C4—C5—C6	119.86 (13)	C8—N2—H2A	109.5
O4—C6—O3	126.49 (14)	C8—N2—H2B	109.5
O4—C6—C5	119.39 (14)	H2A—N2—H2B	109.5
O3—C6—C5	114.12 (13)	C8—N2—H2C	109.5
O2—C7—O1	125.03 (14)	H2A—N2—H2C	109.5
O2—C7—C1	119.97 (13)	H2B—N2—H2C	109.5
O1—C7—C1	114.99 (12)	C7—O1—H1A	114.1 (18)
C13—C8—C9	121.94 (13)	B1—O5—H5	109.5
C13—C8—N2	120.73 (13)	B1—O6—H6	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O3^{i}	0.96 (2)	1.47 (3)	2.429 (2)	173 (2)
N2—H2*A*···O1^{i}	0.89	2.42	2.808 (2)	107
N2—H2*A*···O3^{i}	0.89	2.42	2.835 (2)	109
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Symmetry codes: (i) $x-1/2, -y+3/2, z-1/2$; (ii) $x+1, y, z$; (iii) $-x+1, -y+2, -z$; (iv) $x-2, y, z-1$.